HETEROPHASIC POLYOLEFIN COMPOSITION

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ABSTRACT
Polymer composition suitable for ABS styrenic resin replacement where high dimensional stability and a good esthetical appearance is required, comprising a polymer blend (A), comprising 60-80% by weight, of a crystalline polypropylene homo or copolymer (A1) (MFR <50 g/10 min); and 20-40% by weight, of copolymer(s) of ethylene (A2). Said polymer blend (A) having values of MFR up to 30 g/10 min; the amounts of (A1) and (A2) being referred to the total weight of the polymer blend (A). The polymer composition further comprises 20-40% by weight, of a talc mineral filler (B); the amount of components (B) being referred to the total weight of the composition. Optionally the polymer composition further comprises 1-15% by weight, of an elastomeric polymer (C) different from (A2), having a hardness (Shore A, ASTM D-2240) value equal to or lower than 80 points; the amount of components (C) being referred to the total weight of the composition.
HETEROPHASC POLYOLEFIN COMPOSITION


The present invention relates to heterophasic polyolefin compositions that find application in the production of moulded articles parts, particularly articles obtained by injection moulding, for applications requiring dimensional stability of the mould and high surface quality such as it is required in the field of appliances casing with high esthetical requirements, (e.g. visible parts of white goods, lawn and garden products,) but also for tool boxes, battery cases, toys, luggage where amorphic styrenic polymers are typically used materials. The balance of properties required for replacement of such materials with polyolefin materials is a demanding objective requiring efforts for selecting suitable polymeric structures and components.

In the International application WO2005/014715, polyolefin compositions having flexural modulus values of higher than 1000 MPa, in particular higher than 1100 MPa, still maintaining a good balance of overall mechanical properties and low values of thermal shrinkage are described, comprising (percentage by weight):

(A) from 60 to 85% by weight of a broad molecular weight distribution propylene polymer having a polydispersity index from 5 to 15 and melt flow rate of from 20 to 78 g/10 min, and

(B) from 15 to 40% by weight of a partially xylene-soluble olefin polymer rubber containing at least 65% by weight of ethylene.

In WO2005/121240 specific propylene polymers and ethylene/α-olefin(s) copolymers, optionally in combination with further elastomeric components and a mineral filler characterized in particular by high flexural modulus values, with very low values of thermal shrinkage are disclosed.

The amount of mineral filler (e.g. talc) disclosed in WO2005/121240 is up to 20% by weight of the composition (0.85 and 6% by weight in the examples).

The overall balance of properties is not yet completely satisfying, particularly the mould shrinkage does not reach values comparable to other materials such as styrenic polymers (ABS).

In the international patent application WO2008/079998 talc filled TPO's are disclosed comprising a blend of isotactic propylene with and an elastomeric impact modifier (Engage). The impact modifier is a copolymer obtained by constrained geometry catalyst and the components are selected to obtain low gloss compositions with flexural modulus and HDT of polycarbonate/ABS materials.

It is still felt the need of polyolefin compositions having improved balance of properties particularly thermal shrinkage and surface quality (high gloss homogeneity and scratch resistance) comparable with ABS and PS materials.

Thus, the present invention relates to a polymer composition comprising:

A) a polymer blend, comprising:

A1) 60-80% by weight, preferably 65-75% by weight, of a propylene homopolymer or copolymer containing up to 5% by weight of ethylene and/or one or more C4-C10 α-olefin(s), said homopolymer or copolymer having a value of MFR (230°C, 2.16 kg) of less than 50 preferably from 25 to 40 g/10 min, and a content of fraction soluble in xylene at room temperature (around 25°C) of 7% by weight or less, preferably of 5% by weight or less, even more preferably of 2% by weight or less; and

A2) 20-40% by weight, preferably 25-35% by weight, of one or more copolymer(s) of ethylene with one or more C4-C10 α-olefin(s) containing from 15 to 35% by weight, preferably from 20 to 30% by weight of said C₄-C₁₀ α-olefin(s);

said polymer blend (A) having values of MFR up to 30 g/10 min, preferably of from 10 to 30 g/10 min, more preferably of from 15 to 25 g/10 min, a total content of ethylene of 20% by weight or more, a total content of C₄-C₁₀ α-olefin(s) of equal to or more than 4.5% by weight, preferably of from 5 to 15% by weight, a ratio of the total content of ethylene to the total content of C₄-C₁₀ α-olefin(s) of 2.3 or more, preferably of 3 or more, and an intrinsic viscosity value of the fraction soluble in xylene at room temperature 1.5 dl/g or less, preferably from 1.1 to 1.5 dl/g, the amounts of (A1) and (A2) being referred to the total weight of the polymer blend (A);

B) a talc mineral filler, wherein the amount of component (B) is 20-40% by weight, preferably 22-30% by weight referred to the total weight of the composition.

Optionally and even more preferably the composition according to the present invention further comprises:

a) an elastomeric polymer, different from (A2), having a hardness (Shore A, ASTM D-2240) value equal to or lower than 80 points, preferably equal to or lower than 60 points, more preferably equal to or lower than 55 points; the amount of optional component (A), when present, is 1-1.5% by weight, preferably 2-10% by weight, referred to the total weight of the composition.

From the above definitions it is evident that, when the composition of the present invention comprises the component (A) and (B), the amount of (A) is from 80 to 60% by weight, preferably from 78 to 70% by weight. When it comprises component (A), component (B) and the optional component (C), the amount of (A) is from 79 to 45% by weight, preferably from 76 to 60% by weight with reference to the total weight of the composition.

That is to say a preferred polymer composition according to the present invention is a polyolefin composition comprising component (A) (B) and (C) in the following amounts:

A) 76 to 60% by weight
B) 22-30% by weight
C) 2-10% by weight.

It is also evident that the term “copolymer” includes polymers containing more than one kind of comonomers.

The polyolefin composition of the present invention containing a crystalline propylene polymer component and one or more copolymer(s) of ethylene with C₄-C₁₀ α-olefins, show the required good balance of flexural modulus and Izod impact strength, high surface quality (gloss and scratch resistance) and chemical resistance in contact with organic media (fatty and alcoholic). In addition to the said properties,
the composition of the present invention presents a low degree of mould shrinkage. Said properties impart high dimensional stability and good esthethetical appearance to the final articles obtained from the said composition.

The compositions of the present invention can be easily converted into various kinds of finished or semi-finished articles, in particular by using injection-moulding techniques, as they possess relatively high values of MMR, associated with the above said optimal balance of properties. In particular the compositions exhibit, low mould shrinkage of less than 0.65% (MD) and less than 0.9% (TD), and high gloss of more than 65% (for black samples) and of more than 70%, preferably of more than 80% (for white samples), in addition to an optimal balance of tensile modulus higher than 1500 MPa (ISO 527-1.2); and scratch resistance. The above properties are measured as detailed in the analytical method section.

The filled compositions of the present invention have more preferably and advantageously one or more of the following properties:

- mould shrinkage preferably of less than 0.5% MD and less than 0.75% TD
- a tensile modulus preferably from 1600 to 2200 MPa, more preferably higher than 1800 MPa
- a value of Charpy unnotched impact strength at 23°C (ISO 179/1 eU) preferably from equal to or higher than 40 KJ/m², preferably higher than 100 KJ/m².

The filled compositions of the present invention have preferably a melt volume-flow rate value (MVR—according to ISO 1133) of 15 g/10 min or higher, or even of 20 g/10 min. or higher, for example in the range from 15 to 60 g/10 min., in particular from 20 to 60 g/10 min.

Polymer blend component (A) is a crystalline polymer component (matrix) having typically a very high gloss and Flexural Modulus, preferably a flexural modulus (ISO 178) higher than 900, preferably higher than 950, even more preferably higher than 1000 MPa, and preferably gloss at 60° higher than 90%. The amount of crystalline propylene component (A) which is soluble in xylene at room temperature is, as previously said, equal to or lower than 7% by weight, preferably equal to or lower than 5% by weight, more preferably equal to or lower than 2% by weight. Such values of xylene-soluble content correspond to isostatic index values equal to or higher than 93%, preferably equal to or higher than 95%.

Typically the copolymer(s) of ethylene component (A2) (rubber) is partially soluble in xylene at room temperature. The fraction of component (A2) which is soluble in xylene at room temperature is preferably of about 50-87% by weight, more preferably 50-70% by weight of component (A2).

Preferably, the polymer blend component (A) according to the present invention has a DSC thermogram profile showing a melting temperature peak (Tm,2) of from 80 to 140°C, preferably from 100 to 125°C, distinguishable from a DSC melting temperature peak (Tm,1) at higher temperatures equal to or higher than 140°C, preferably equal to or higher than 150°C, more preferably higher than 160°C. Without being bound by any theory the Tm,2 is attributed to the ethylene crystallinity (insoluble fraction) of component (A2), Tm,1 is attributed to the propylene crystallinity of component (A1). The DSC thermogram is collected according to the method described in the analytical method section.

Illustrative examples of copolymers for components (A1) and (A2) include 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene and 1-octene, with 1-butene being particularly preferred.

The composition of the present invention can be prepared by mechanically mixing components (C) and (B), when present, with the polymer blend (A). Such polymer blend (A) can in turn be prepared by mechanical blending (A1) and (A2) or preferably by a sequential polymerization, comprising at least two sequential steps, wherein components (A1) and (A2) are prepared in separate subsequent steps, operating in each step in the presence of the polymer formed and the catalyst used in the preceding step. The catalyst is added only in the first step, however its activity is such that it is still active for all the subsequent steps.

The polymerization, which can be continuous or batch, is carried out following known techniques and operating in liquid phase, in the presence or not of inert diluent, or in gas phase, or by mixed liquid-gas techniques. It is preferable to carry out the polymerization in gas phase.

Reaction time, pressure and temperature relative to the polymerization steps are not critical, however it is best if the temperature is from 50 to 100°C. The pressure can be atmospheric or higher.

The regulation of the molecular weight is carried out by using known regulators, hydrogen in particular.

The polymer blend (A) can also be produced by a gas-phase polymerisation process carried out in at least two interconnected polymerisation zones. The said type of process is illustrated in European patent application 782 587.

The said polymerizations are preferably carried out in the presence of stereospecific Ziegler-Natta catalysts. An essential component of said catalysts is a solid catalyst component comprising a titanium compound having at least one titanium-halogen bond, and an electron-donor compound, both supported on a magnesium halide in active form. Another essential component (co-catalyst) is an organoaluminium compound, such as an aluminium alkyl compound.

An external donor is optionally added.

The catalysts generally used in the process of the invention are capable of producing polypropylene with an isotactic index equal to or greater than 93%, preferably equal to or greater than 95%. Catalysts having the above mentioned characteristics are well known in the patent literature; particularly advantageous are the catalysts described in U.S. Pat. No. 4,399,054 and European patent 45977. Other examples can be found in U.S. Pat. No. 4,472,524.

The solid catalyst components used in said catalysts comprise, as electron-donors (internal donors), compounds selected from the group consisting of ethers, ketones, lactones, compounds containing N, P and/or S atoms, and esters of mono- and dicarboxylic acids.

The internal donor is preferably selected from the esters of mono or dicarboxylic organic acids such as benzoates, malonates, phthalates and certain succinates. They are described in U.S. Pat. No. 4522930, European patent 45977 and international patent applications WO 00/63261 and WO 01/57099, for example. Particularly suited are the phthalic acid esters and succinate acids esters. Alkylphthalates are preferred, such as diisobutyl, dioctyl and diphenyl phthalate and benzyl-butyl phthalate.

Representative examples of said diesters are 2-methyl-2-isopropyl-1,3-dimethoxycarpropane, 2,2-diisobutyl-1,3-dimethoxycarpropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxycarpropane, 2-isopropyl-2-isomethyl-1,3-dimethoxycarpropane, 9,9-bis(methoxymethyl)fluorene.
Other suitable electron donors are succinates, preferably selected from succinates of formula (I) below:

wherein the radicals $R_1$ and $R_2$ equal to, or different from, each other are a $C_1$-$C_{20}$ linear or branched alkyl, alkenyl, cycloalkyl, aryl, aralkyl or alkylaryl group, optionally containing heteroatoms; the radicals $R_3$ to $R_6$ equal to, or different from, each other, are hydrogen or a $C_1$-$C_{20}$ linear or branched alkyl, alkenyl, cycloalkyl, aryl, aralkyl or alkylaryl group, optionally containing heteroatoms, and the radicals $R_7$ to $R_9$ which are joined to the same carbon atom can be linked together to form a cycle; with the proviso that when $R_7$ to $R_9$ are contemporaneously hydrogen, $R_8$ is a radical selected from primary branched, secondary or tertiary alkyl groups, cycloalkyl, aryl, aralkyl or alkylaryl groups having from 3 to 20 carbon atoms; or of formula (II) below:

wherein the radicals $R_1$ and $R_2$ equal to or different from each other, are a $C_1$-$C_{20}$ linear or branched alkyl, alkenyl, cycloalkyl, aryl, aralkyl or alkylaryl group, optionally containing heteroatoms and the radical $R_3$ is a linear alkyl group having at least four carbon atoms optionally containing heteroatoms.

Other electron-donors suitable are 1,3-diethers. Suitable diethers are described in published European patent applications 361933 and 728769.

The preparation of the above mentioned catalyst components is carried out according to various methods.

For example, a $MgCl_2$-nROH adduct (in particular in the form of spheroidal particles) wherein n is generally from 1 to 3 and ROH is ethanol, butanol or isobutanol, is reacted with an excess of TiCl$_4$ containing the electron-donor compound. The reaction temperature is generally from 80 to 120°C. The solid is then isolated and reacted once more with TiCl$_4$, in the presence or absence of the electron-donor compound, after which it is separated and washed with aliquots of a hydrocarbon until all chlorine ions have disappeared.

In the solid catalyst component the titanium compound, expressed as Ti, is generally present in an amount from 0.5 to 10% by weight. The quantity of electron-donor compound which remains fixed on the solid catalyst component generally is 5 to 20% by moles with respect to the magnesium dichloride.

The titanium compounds which can be used for the preparation of the solid catalyst component are the halides and the halogen alkoxides of titanium. Titanium tetrachloride is the preferred compound.

The reactions described above result in the formation of a magnesium halide in active form. Other reactions are known in the literature, which cause the formation of magnesium halide in active form starting from magnesium compounds other than halides, such as magnesium carboxylates.

The Al-alkyl compounds used as co-catalysts comprise the Al-trialkyls, such as Al-triethyl, Al-triisobutyl, Al-tri-n-butyl, and linear or cyclic Al-alkyl compounds containing two or more Al atoms bonded to each other by way of O or N atoms, or SO$_4$ or SO$_2$ groups.

The Al-alkyl compound is generally used in such a quantity that the Al/Ti ratio be from 1 to 1000.

The electron-donor compounds that can be used as external donors include aromatic acid esters such as alkyl benzoates, and in particular silicon compounds containing at least one Si—OR bond, where R is a hydrocarbon radical.

Examples of silicon compounds are (tert-butyl)$_2$Si (OCH$_3$)$_2$, (cyclohexyl)(methyl)Si (OCH$_3$)$_2$, (phenyl)Si (OCH$_3$)$_2$, and (cyclopentyl)SiOCH$_3$)$_2$. 1,3-diethers having the formulae described above can also be used advantageously. If the internal donor is one of these diethers, the external donors can be omitted.

The catalysts can be pre-contacted with small amounts of olefins (prepolymerization).

Component (C) when present is preferably selected from copolymers of ethylene with a $C_3$-$C_{20}$ α-olefin containing at least 20 wt%, preferably from 20 to 70 wt% of $C_3$-$C_{20}$ α-olefin (13C-NMR analysis). Suitable and preferred copolymers component (C) commercially available are obtained with metallosene or constrained geometry catalysis and typically have molecular weight distribution (Mw/Mn measured via GPC) of from 1 to 3.

Preferred examples of elastomeric polymers component (C) are:

(a) elastomeric copolymers of ethylene with 1-octene having from 20 wt% to 45 wt% of 1-octene (13C-NMR analysis); preferably having density of less than 0.89 g/ml (measured according to ASTM D-792);

(b) elastomeric thermoplastic copolymers of ethylene with 1-butene having from 20 wt% to 40 wt% of 1-butene (13C-NMR analysis); preferably having density of less than 0.89 g/ml (measured according to ASTM D-792);

A specific example of copolymers (b) is ethylene-butene 1 and random copolymer rubber ENGAGE 7467 produced by The Dow Chemical Co. Ltd., having density of 0.862 g/cm$^3$ according to method ASTM D 792, MFR of 1.2 g/10 min (ASTM D 1238 190°C C/2,16 Kg, standard technically equivalent to ISO 1133), hardness Shore A (ASTM D-2240) of 52. The alchen filler component (B), preferred pure white, used in the composition of the present invention is typically a Magnesium-Silicate-Hydrate with lamellar structure (platy) in particle form having an average (d50) diameter ranging form 0.1 to 10 micrometers and a top cut ranging from 1 to 40 micrometer, more preferably the average (d50) diameter is equal to or lower than 5 micrometer (determination ISO 13317-3 by Sedigraph).

The composition of the present invention can also contain additives commonly employed in the art, such as antioxidants and process stabilisers, light stabilisers, release agents, antistatics, nucleating agents and colorants.

As previously said, the compositions of the present invention can be prepared by blending the components (A), (B) and optionally (C). Any mixing apparatus equipped with mixing elements and known in the art can be used, such as an internal mixer or extruder. For example one can use a Banbury
mixer or single-screw Buss extruder or twin-screw Maris or Werner & Pfleiderer type extruder.

[0065] The present invention also provides final injection molded articles, such as appliances casing with high esthetical requirements, (e.g. visible parts of white goods, lawn and garden products,) but also for tool boxes, battery casing, toys, luggage made of the said polyolefin composition.

[0066] The practice and advantages of the present invention are disclosed below in the following examples. These Examples are illustrative only, and are not intended to limit the scope of the invention in any manner whatsoever.

[0067] The following analytical methods are used to characterize the polymer compositions.

[0068] Melt mass-Flow Rate (MFR) and Melt Volume-flow Rate (MVR): measured according to ISO 1133 at 230°C, 1.2 Kg were not differently specified.

[0069] Ash content (1 h/625°C): ISO 3451/1

[0070] [I.V.] intrinsic viscosity: determined in tetrahydrofuran at 135°C.


[0073] Tensile properties: Tensile Modulus, Tensile stress and strain at yield and Tensile stress and strain at break determined according to ISO 527.

[0074] Charpy notched impact test: ISO 179/1 eA at 23°C and 0°C.

[0075] Charpy unnotched impact test: ISO 179/1 eU at 23°C and 0°C.

[0076] Izod Impact test: ISO 180 at 23°C and 0°C.

[0077] Xylene soluble and insoluble fractions

[0078] 2.5 g of polymer and 250 cm³ of xylene are introduced in a glass flask equipped with a refrigerator and a magnetic stirrer. The temperature is raised in 30 minutes up to the boiling point of the solvent. The so obtained clear solution is then kept under reflux and stirring for further 30 minutes. The closed flask is then kept for 30 minutes in a bath of ice and water and at 25°C for 30 minutes as well. The so formed solid is filtered on a quick cutting paper and the filtered liquid is poured in a previously weighed aluminium container which is heated on a heating plate under nitrogen flow, to remove the solvent by evaporation. The container is then kept in an oven at 80°C under vacuum until constant weight is obtained. The weight percentage of polymer soluble in xylene at room temperature (25°C) is then calculated.

[0079] The percent by weight of polymer insoluble in xylene at room temperature is considered the isotacticity index of the polymer. This value corresponds substantially to the isotacticity index determined by extraction with boiling n-heptane, which by definition constitutes the isotacticity index of polypropylene.

Thermal Properties (DSC):

[0080] The melting temperatures (Tm,α) and (Tm,β) are measured on the polymer composition (A). Differential scanning calorimetry (DSC) is used according to ISO 11357/3 with samples of 5-7 mg weight; heating and cooling rates 20°C/min, in a temperature operating range from 40°C to 200°C.

[0081] Longitudinal (MD) and transversal (TD) mould shrinkage: measured after 24 h on DIN AS/4 mm plaques and a film gate over the whole width to ensure homogeneous flow and orientation of the melt. A plaque of 210x145x4 mm is moulded in an injection moulding machine "SANDRETTO serie 7 190" (where 190 stands for 190 tons of clamping force).

The Injection Conditions are:

[0082] melt temperature: 210°C;

[0083] Injection moulding pressure: 80 bar

[0084] mould temperature: 30°C;

[0085] injection time: 11 seconds;

[0086] holding pressure: 50 bar

[0087] holding time: 30 seconds;

[0088] Cooling time: 20 sec

[0089] Cycle time: 76 s

[0090] Screw speed: 30 rpm (1/min)

[0091] The plaque is measured 24 hours after moulding (mould shrinkage) and after annealing 48 h at 80°C. (Total shrinkage), through callipers, and the shrinkage is given by:

\[
\text{Longitudinal shrinkage (MD)} = \frac{210 - \text{read value}}{210} \times 100
\]

\[
\text{Transversal shrinkage (TD)} = \frac{145 - \text{read value}}{145} \times 100
\]

wherein 210 is the length (in mm) of the plaque along the flow direction (MD), measured immediately after moulding; 145 is the length (in mm) of the plaque crosswise the flow direction (TD), measured immediately after moulding; the read value is the plaque length in the relevant direction. Data are reported in table 3.

[0092] Gloss on plaque: specular gloss (also called Gardner gloss) determined according to ISO 2813 with 60° Geometry on high gloss plaques 1 mm thickness.

10 rectangular specimens (55x30x1 mm) for each polymer to be tested are injection molded using a Krauss Maffei injection moulding machine model KM 150-700C operated under the following conditions:

[0093] Melt temperature: 200°C.

[0094] Melt temperature profile: Zone1 180°C, Zone2 185°C, Zone3 190°C,

[0095] Zone4 190°C, injector 190°C.

[0096] Mould temperature: 30°C.

[0097] Injection moulding pressure: 48 bar

[0098] Back pressure: 15 bar

[0099] Injection speed: 95 mm/s

[0100] Injection time: 0.22 s

[0101] holding pressure: 80 bar

[0102] holding time: 10 sec

[0103] Cooling time: 15 sec

[0104] Cycle time 36 s

[0105] Screw speed 80 rpm (1/min)

[0106] The value of the injection pressure should be sufficient to completely fill the mould in the above mentioned indicated time span.

[0107] By a glossmeter the fraction of luminous flow reflected by the examined specimens surface is measured, under an incident angle of 60°. The value reported in table 2 corresponds to the mean gloss value over 10 specimens for each tested polymer.

[0108] The glossmeter used is a photometer Zeihtner model ZGM 1020 or 1022 set with an incident angle of 60°. The measurement principle is given in the Norm ASTM D2457. The apparatus calibration is done with a sample having a known gloss value. Data are reported in table 3.
Scratch resistance was measured with Erichson 5 finger scratch testing system, with 10N load on DIN A5 plaques.

The Erichson scratch tester allows the evaluation of scratch resistance at forces between 5N and 20N. In the test a force of 10N was applied (inferior loads did not produce significant scratches) at a speed of 1000 mm/min of the scratch tool. The tool is in contact with the surface through a round shaped tip with a diameter of 1 mm. A pattern of 20 lines (10 in one direction and 10 at right angles to those) is generated by the tester and the scratch resistance is determined afterwards by measuring the difference in brightness of the scratched and the unscratched surface. The difference in brightness is measured by a BYK Gardner instrument (or equivalent photometer) and the resulting delta L (dL) value (CIE Lab system) OMS is in direct correlation with scratch depth. Thus, dl is used as an indicator of the scratch resistance of the compounds.

3 plaques of different ground surface (coarse grain, fine grain, smooth) were prepared for each polymer to be tested. Plaques were injection molded using a Krauss Maffei injection moulding machine model KM 150-700C2 operated under the following conditions:

Melt temperature: 210°C.
Injection moulding profile: Zone 1 190°C, Zone 2 200°C, Zone 3 210°C, Zone 4 210°C, Zone 5 210°C, injector 210°C.
Mould temperature: 30°C.
Injection moulding pressure: 80 bar
Back pressure: 10 bar
Injection speed: 7 mm/s
Injection time: 11 s
Holding pressure: 50 bar
Holding time: 30 sec
Cooling time: 20 sec
Cycle time: 76 s

The plaques were submitted to the scratch test data are reported in table 3.

### EXAMPLES

Polymer blend component (A) was produced in a plant operating continuously according to the mixed liquid-gas polymerization technique, carried out under the conditions specified in Table 1. The polymerization was carried out in the presence of a catalyst system in a series of two reactors equipped with devices to transfer the product from one reactor to the one immediately next to it.

#### Polymerization Example A

The polymerisation run is conducted in continuous in a series of two reactors equipped with devices to transfer the product from one reactor to the one immediately next to it. The first reactor is a liquid phase reactor, and the second reactor is a fluid bed gas phase reactor. Polymer component A1 (matrix) is prepared in the first reactor, while polymer component A2 (rubber) is prepared in the second reactor.

Temperature and pressure are maintained constant throughout the course of the reaction. Hydrogen is used as molecular weight regulator. The gas phase (propylene, ethylene, butene and hydrogen) is continuously analysed via gas chromatography. Process conditions are reported in the table 1.

At the end of the run the powder is discharged and dried under a nitrogen flow.

The data relating to Xylene soluble and non-monomer content in the final polymer composition reported in table 2 are obtained from measurements carried out on the so obtained polymers, stabilized when necessary.

Then the polymer particles are introduced in an extruder, wherein they are mixed with a conventional additive package comprising 1800 ppm of a DMDBS clarifier/nucleating agent (Millad 3988) to obtain a nucleated composition.

The polymer particles are extruded under nitrogen atmosphere in a twin screw extruder, at a rotation speed of 250 rpm and a melt temperature of 200-250°C.

The data relating to the other physical-mechanical properties of the final polymer blend composition (A) are also reported in table 2.

### TABLE 1

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEAL/propylene</td>
<td>0.17</td>
</tr>
<tr>
<td>TEAL/DCPMS</td>
<td>molar ratio 3</td>
</tr>
<tr>
<td>liquid phase reactor: homopolymer (matrix) A1</td>
<td></td>
</tr>
<tr>
<td>Polymerisation temperature, °C</td>
<td>70</td>
</tr>
<tr>
<td>Pressure, Mpa</td>
<td>37</td>
</tr>
<tr>
<td>Residence time, min</td>
<td>105</td>
</tr>
<tr>
<td>H₂ bulk feed, mol ppm</td>
<td>3600</td>
</tr>
<tr>
<td>MFR (230°C/2.16 Kg) g/10 min</td>
<td>31</td>
</tr>
<tr>
<td>Xylene soluble fraction in (A1) wt %</td>
<td>2</td>
</tr>
<tr>
<td>Split wt %</td>
<td>69</td>
</tr>
<tr>
<td>Gas phase reactor: ethylene butene copolymer A2 (rubber)</td>
<td></td>
</tr>
<tr>
<td>Polymerisation temperature, °C</td>
<td>86</td>
</tr>
<tr>
<td>Pressure, bar</td>
<td>16</td>
</tr>
<tr>
<td>Residence time, min</td>
<td>50</td>
</tr>
<tr>
<td>H₂/C₅⁻ mol ratio</td>
<td>0.22</td>
</tr>
<tr>
<td>C₅⁻ (C₄⁺ + C₅⁺) Mol ratio</td>
<td>0.42</td>
</tr>
<tr>
<td>Split wt %</td>
<td>31</td>
</tr>
<tr>
<td>Butene-1 in the rubber (A2) calculated wt %</td>
<td>24</td>
</tr>
<tr>
<td>Xylene soluble in (A2) calculated wt %</td>
<td>63%</td>
</tr>
</tbody>
</table>

Notes:
- H₂ bulk = hydrogen concentration in the liquid monomer;
- C₅⁻ = ethylene;
- C₄⁺ = propylene;
- C₅⁺ = butene-1.

The polymer composition (A) prepared was mechanically mixed with components (B) in example 1, 4 and 6, and with component (B) and (C) in example 5, 7 and 8 by extrusion under the previously described conditions. A Colorant and a conventional additives package comprising anti-oxidants, light and heat stabilizers, antimics and release agents (e.g. Erucamide) was also mixed in the composition in
the proportions reported in Table 3. The properties of the so obtained final compositions are also reported in Table 3.

**Added Components**

- **Engage 7467**: (see description page 3) used as optional component (C);
- **Talc HM4 produced by IMI Fabi**: pure white talc powder with average particle size (Median diameter D50) of about 10 μm, used as component (B);
- **Talc Jetfine 3 CA produced by Rio Tinto Minerals**: pure white fine talc powder with average particle size (D50) of about 1 μm, (compacted) used as component (B);
- **Conventional additives package**
- Black color: BK MB-Colcolor E30/90 (Degussa)
- White color: Titandioxide-TI-PURE R-104 (coated white blue shade Titandioxide)
- Other polymer blends (heterophase compositions HECO2 and HECO 3) are used instead of component (A) in the comparative examples. Structures and properties of the comparative polymer blends are reported in Table 2.

**Comparative Examples 2c and 3c**

Example 1 was repeated blending instead of component (A) according to the invention, a different polymer blend respectively HECO 2 in example 2c, and HECO 3 in example 3c

**Reference Example Ref 1**

**Reference Example Ref 2**

The polymer blend component (A) with the sole addition of a black colorant and the addition package is reported for reference.

**Reference Example Ref 3**

The polymer blend component (A) with the sole addition of a white colorant and the addition package is reported for reference.

**Reference Example Ref 4**

The properties of the so obtained final compositions are also reported in Table 3.

**Table 2**

<table>
<thead>
<tr>
<th>POLYMER BLENDS</th>
<th>A</th>
<th>HECO2</th>
<th>HECO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix component type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matrix MFR</td>
<td>g/10 min</td>
<td>31</td>
<td>28</td>
</tr>
<tr>
<td>(230° C/2.16 Kg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XS fraction in the matrix</td>
<td>wt %</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Rubber component type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2 wt % referred to</td>
<td>wt %</td>
<td>31</td>
<td>18</td>
</tr>
<tr>
<td>the rubber component</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymer Blend properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt index (MFR)</td>
<td>g/10 min</td>
<td>16.8</td>
<td>15</td>
</tr>
<tr>
<td>(230° C/2.16 Kg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xylene-soluble fraction</td>
<td>wt %</td>
<td>20</td>
<td>17.0</td>
</tr>
<tr>
<td>LI. of xylene-soluble</td>
<td>dL/g</td>
<td>1.4</td>
<td>2.6</td>
</tr>
<tr>
<td>Ethylene content</td>
<td>wt %</td>
<td>24.2</td>
<td>9.0</td>
</tr>
<tr>
<td>Butene content</td>
<td>wt %</td>
<td>76.8</td>
<td>—</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>MPa</td>
<td>1036</td>
<td>1133</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>MPa</td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>Iodized impact resistance at 23°C (ISO 180)</td>
<td>kJ/m²</td>
<td>22.5</td>
<td>7.6</td>
</tr>
<tr>
<td>at 0° C, kJ/m²</td>
<td></td>
<td>6.8</td>
<td>5.2</td>
</tr>
<tr>
<td>at -20° C, kJ/m²</td>
<td></td>
<td>3.7</td>
<td>4.2</td>
</tr>
<tr>
<td>DB/B transition temperature</td>
<td>°C</td>
<td>-47.5</td>
<td>&lt;= 50</td>
</tr>
</tbody>
</table>

**Table 3**

<table>
<thead>
<tr>
<th>EXAMPLES (BLACK)</th>
<th>1</th>
<th>2C</th>
<th>3C</th>
<th>REF. 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (A)</td>
<td>wt %</td>
<td>72.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative HECO2</td>
<td>wt %</td>
<td>72.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comparative HECO3</td>
<td>wt %</td>
<td>72.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Component (B) Talc HM4</td>
<td>wt %</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
</tr>
<tr>
<td>Conventional additives package</td>
<td>wt %</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>Black color</td>
<td>wt %</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Sum of components wt %</td>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Melt index (MFR) (23° C/2.16 Kg)</td>
<td>ISO 1133</td>
<td>17.4</td>
<td>14.7</td>
<td>15</td>
</tr>
<tr>
<td>Density (23° C.)</td>
<td>ISO 1183</td>
<td>1.093</td>
<td>1.077</td>
<td>1.084</td>
</tr>
</tbody>
</table>

**Method**

- Unit
- g/10 min
- g/cm³

**Note:** For the comparative polymer blends, the properties are reported in Table 2.
### TABLE 3-continued

<table>
<thead>
<tr>
<th>Property</th>
<th>ISO 527-1, 2</th>
<th>ISO 179/1eU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile modulus</td>
<td>1960 (23°C)</td>
<td>49.6 (kN/m²)</td>
</tr>
<tr>
<td></td>
<td>2610 (0°C)</td>
<td>33.1 (kN/m²)</td>
</tr>
<tr>
<td></td>
<td>2150 (Mo)</td>
<td>0.6 (in-flow)</td>
</tr>
<tr>
<td></td>
<td>1090 (Sh)</td>
<td>0.8 (in-flow)</td>
</tr>
<tr>
<td>Mould shrinkage after 24 h</td>
<td>0.84 (cross-flow)</td>
<td>0.96 (in-flow)</td>
</tr>
<tr>
<td>Total shrinkage after annealing</td>
<td>0.7 (in-flow)</td>
<td>0.96 (in-flow)</td>
</tr>
<tr>
<td>Gloss (1 mm) Geometry 60</td>
<td>ISO 2813 %</td>
<td>68.4</td>
</tr>
<tr>
<td>Surface evaluation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile test at 23°C. ISO 527-1, 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charpy unnotched impact strength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scratch test (10N) on DIN A 5 plaque, grained</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coarse grain</td>
<td>dL 1</td>
<td>6.4</td>
</tr>
<tr>
<td>Fine grain</td>
<td>dL 1.4</td>
<td>8.2</td>
</tr>
<tr>
<td>Smooth</td>
<td>dL 0.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Examples (white)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition (A)</td>
<td>wt % 72.80</td>
<td>67.80</td>
</tr>
<tr>
<td>Component (C) (Engage 7467)</td>
<td>wt % 5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>Component (B) Talk IMI Pab HM 4</td>
<td>wt % 25.00</td>
<td>25.00</td>
</tr>
<tr>
<td>Conventional additives package</td>
<td>wt % 1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>White color</td>
<td>wt % 1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

1. A polymer composition comprising:
A) a polymer blend, comprising:
   A1) 60-80% by weight, of a crystalline propylene homopolymer or copolymer containing up to 5% by weight of ethylene and/or at least one C₄-C₁₀ α-olefin, said homopolymer or copolymer having a value of MFR (230°C, 2.16 kg) of at most 50 g/10 min, and a content of fraction soluble in xylene at room temperature of at most 1.5 dl/g, the amounts of (A1) and (A2) being referred to the total weight of the polymer blend (A); and
   B) a talc mineral filler; wherein the amount of component (B) is 20-40% by weight referred to the total weight of the composition.
B) 20-40% by weight, of at least one copolymer of ethylene with at least one C₄-C₁₀ α-olefin containing from 15 to 35% by weight, of said C₄-C₁₀ α-olefin; said polymer blend (A) having values of MFR up to 30 g/10 min; a total content of ethylene of at least 20% by weight; a total content of C₄-C₁₀ α-olefin(s) of at least 4.5% by weight; a ratio of the total content of ethylene to the total content of C₄-C₁₀ α-olefin(s) of at least 2.3, and an intrinsic viscosity value of the fraction soluble in xylene at room temperature of at most 1.5 dl/g, the amounts of (A1) and (A2) being referred to the total weight of the polymer blend (A); and
C) an elastomeric polymer different from (A2), having a hardness (Shore A, ASTM D-2240) value of at most 80; wherein the amount of component (C) is 1-15% by weight referred to the total weight of the composition.
2. The polymer composition according to claim 1 further comprising:
C) an elastomeric polymer different from (A2), having a hardness (Shore A, ASTM D-2240) value of at most 80; wherein the amount of component (C) is 1-15% by weight referred to the total weight of the composition.
3. The polymer composition according to claim 2 comprising:
A) 76 to 60% by weight of a polymer blend comprising:
   A1) 60-80% by weight, of a crystalline propylene homopolymer or copolymer containing up to 5% by weight of ethylene and/or at least one C₄-C₁₀ α-olefin,
said homopolymer or copolymer having a value of MFR (230°C, 2.16 kg) of at most 50 g/10 min, and a content of fraction soluble in xylene at room temperature (around 25°C) of at most 7% by weight; and
A) 20-40% by weight, of at least one copolymer of ethylene with at least one C₃-C₁₀ α-olefin containing from 15 to 35% by weight, of said C₃-C₁₀ α-olefin(s); said polymer blend (A) having values of MFR up to 30 g/10 min; a total content of ethylene of at least 20% by weight; a total content of C₃-C₁₀ α-olefin(s) of at least 4.5% by weight; a ratio of the total content of ethylene to the total content of C₃-C₁₀ α-olefin(s) of at least 2.3, and an intrinsic viscosity value of the fraction soluble in xylene at room temperature of at most 1.5 dl/g, the amounts of (A1) and (A2) being referred to the total weight of the polymer blend (A);
B) 22-30% by weight of a talc mineral filler; and
C) 2-10% by weight of an elastomeric polymer different from (A2), having a hardness (Shore A, ASTM D-2240) value of at most 80.

4. The composition according to claim 2 wherein component (C) has a molecular weight distribution (Mw/Mn measured via GPC) of from 1 to 3.

5. The composition according to claim 2 wherein component (C) is selected from copolymers of ethylene with a C₃-C₁₀ α-olefin containing at least 20 wt% of units derived from said C₃-C₁₀ α-olefin.

6. The composition according to claim 5 wherein component (C) is selected from the group consisting of:
   (a) elastomeric copolymers of ethylene with 1-octene having from 20 wt % to 45 wt % of 1-octene (13C-NMR analysis), and
   (b) elastomeric thermoplastic copolymers of ethylene with 1-butene having from 20 wt % to 40 wt % of 1-butene (13C-NMR analysis).

7. The polymer composition according to claim 1 wherein the polymer blend component (A) has a DSC thermogram profile showing a melting temperature peak (Tm_d) of from 80 to 140°C, distinguishable from a DSC melting temperature peak (Tm_t) equal to or higher than 140°C.

8. Moulded articles comprising the polymer composition according to claim 1.

* * * * *